Polyoxometalates

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Self-Assembly of a Giant Tetrahedral 3d–4f Single-Molecule Magnet within a Polyoxometalate System

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Dedicated to Professor Manfred Scheer on the occasion of his 60th birthday

Abstract: *A giant tetrahedral heterometallic polyoxometalate (POM) $[Dy_{30}Co_8Ge_{12}W_{108}O_{408}(OH)_{42}(OH_2)_{30}]^{56-}$, which shows single-molecule magnet (SMM) behavior, is described. This hybrid contains the largest number of 4f ions of any polyoxometalate (POM) reported to date and is the first to incorporate two different 3d–4f and 4f coordination cluster assemblies within same POM framework.*

Supramolecular self-assembly is a synthetic strategy that relies on the components in a reaction system finding a local energy minimum to stabilize a molecular assembly. This can lead to spectacular structures that cannot be made by any other means.[1,2] Polyoxometalates (POMs) are anionic, nanosized metal–oxygen clusters of transition metals in high oxidation states, such as Mo^{VI}, W^{VI}, and V^{V}, which also form by self-assembly. Targeted POM synthesis can be achieved by careful variation of the synthesis conditions, for example, concentration of reagents, solvent, pH, counterions, and temperature.[3] There is growing interest in the use of POMs as "super ligands" for polynuclear transition metals, owing to their potential applications in catalysis, magnetism, and biological systems.[4] A particularly fascinating area concerns encapsulating larger aggregations of 3d transition metals.[5] The construction of high-nuclearity lanthanide-containing POMs proves more difficult because lanthanide ions have variable and usually higher coordination numbers than 3d cations and exhibit low stereochemical preferences as a result of the small energy differences between various coordination geometries.[6] Although there are now many POMs that are all 3d-[4,5] or all 4f-substituted[7–12] that have been characterized, very few heterometallic 3d–4f systems have been reported, and only a few in which the 3d and 4f ions are connected to each other,[13–25] but rather the 3d and 4f centers are spatially separated and magnetically isolated. The strong oxophilic preferences of the 4f ions towards POMs may hinder formation of 3d–4f aggregates and their capture by POM super ligands. Also, the larger size of 4f ions usually restricts their ability to act as linkers between lacunary POM units, resulting in polymeric or unusually large molecular POM assemblies.[7–12,26–28] Successful attempts to achieve 3d–4f clusters within a POM framework have demanded a number of different synthetic strategies, such as the use of pre-synthesized heterometallic clusters as precursors for reaction with lacunary species[15,16] or the addition of co-ligands to assist in the formation of 3d–4f POM systems.[17,24] In another approach, 3d-substituted Weakley-type dimers were reacted in the presence of 4f ions to substitute the labile outer $M(H_2O)$ groups in sandwich-type POMs, $([M_4(H_2O)_2(GeW_9O_{34})_2]^{n-}$; $M = Mn^{II}$, Cu^{II}).[18,19] Thus, the formation of anisotropic, high-spin 3d–4f-containing POMs has remained a demanding task for chemists, and one that we have eagerly pursued.

A further inspiration is the recent burgeoning of the area of 3d–4f coordination cluster compounds and their relevance for molecular magnetism,[29,30] and in particular the area of single molecule magnets (SMMs). SMMs are molecules showing slow relaxation of their magnetization below a blocking temperature (T_B). The rational synthesis of SMMs achieving high T_B values is an interesting challenge for synthetic chemists,[31] but a recent strategy has been to combine of 3d and 4f ions within the same molecule since these can provide mixed coupling and relaxation pathways[32] and the 3d ions can provide significant spin (S) whilst 4f ions such as Dy^{III}, Tb^{III}, and Ho^{III} contribute the significant anisotropy necessary to hinder spin inversion. The field of POM-based SMMs is relatively new, with only a few SMMs having been reported to date,[22,33–43] and the $[ErW_{10}O_{36}]^{9-}$ polyanion is the first example (2008) of a POM exhibiting SMM behavior.[32]

We have carried out a systematic investigation to explore new routes to preparing novel 3d–4f heterometallic clusters stabilized by POM ligands with a view to developing new types of clusters showing SMM behavior and we report herein on the 3d–4f $[\{(GeW_9O_{34})_2Dy^{III}_3(\mu\text{-}OH)_3(H_2O)\}_6\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}_4]^{56-}$ nanocluster polyanion (**1**), which contains 30 Dy^{III}, 8 Co^{II}, and 108 W^{VI} metal centers per polyanionic cluster unit and shows SMM behavior.

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The polyanion **1** was isolated as the hydrated mixed cesium–sodium–cobalt salt $Cs_{14}Co_6Na_{30}[\{(GeW_9O_{34})_2Dy^{III}_3(\mu_2\text{-}OH)_3(H_2O)_2\}_6\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}_4]\cdot ca.\,370\,H_2O$ (**CsCoNa-1**) and was synthesized by a straightforward self-assembly process in aqueous solution. Not all the countercations and waters could be located in the crystal structure as when these are remote from the clusters they become heavily disordered, but the above formulation is in good agreement with the microanalytical data. The polyanion **1** is by far the largest discrete heterometallic polyoxotungstate and contains the largest number of dysprosium centers so far reported in a POM. It possesses a topology new to POM chemistry which can be described in terms of a hollow giant tetrahedral motif. The architecture of this highly negatively charged, giant POM aggregate is based on the combination of two different structural components. The first of these embodies a motif from sandwich-type POM chemistry. The other constitutes a hydroxo-bridged 3d–4f aggregation familiar from coordination cluster chemistry. The overall nanocluster polyanion thus represents the fusion of these two areas of inorganic chemistry.

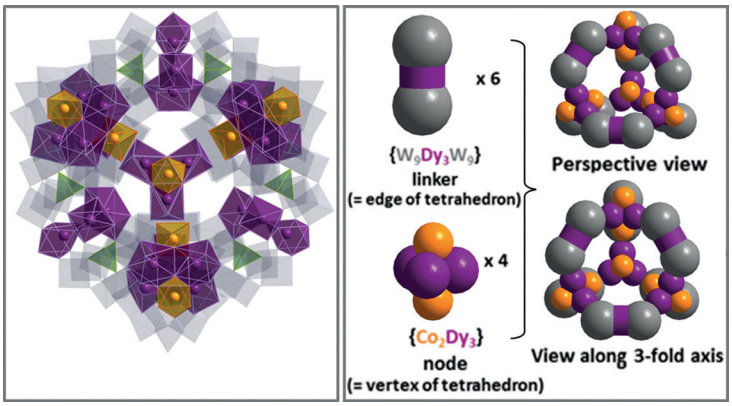

Figure 1. Left: Polyhedral representation of **1**. Color code: WO_6 octahedra gray, GeO_4 tetrahedra green, CoO_6 orange, DyO_x purple. Right: Model showing how the $\{W_9Dy_3W_9\}$ and $\{Co_2Dy_3\}$ building blocks build up the giant tetrahedral topology of the polyanion **1**.

The structure of the nanocluster polyanion **1** (Figure 1) is composed of six anionic sandwich-type building blocks where a planar triangular $\{Dy^{III}_3(\mu\text{-}OH)_3(OH_2)\}^{6+}$ unit is sandwiched by two trilacunary $[A\text{-}\alpha\text{-}GeW_9O_{34}]^{10-}$ anions. Similar trinuclear lanthanide motifs are observed in some lanthanide-containing sandwich-type POMs,[44] but usually a carbonate anion is encapsulated within the trinuclear moiety.[44c–h] The $\{(GeW_9O_{34})_2Dy^{III}_3(\mu\text{-}OH)_3(H_2O)\}$ units are linked together by four cationic trigonal-bipyramidal 3d–4f $\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}^{7+}$ coordination clusters. Thus, each dimeric subunit links two $\{Co_2Dy_3\}$ clusters (Figure 1; Supporting Information, Figure S1) whilst each $\{Co_2Dy_3\}$ is coordinated by three dimeric Keggin moieties, resulting in an assembly with idealized T_d symmetry (Figure 2c). Two Dy centers in the $\{Dy_3\}$ units have regular trigonal-prismatic coordination geometry from two bridging hydroxo ligands and four terminal oxido ligands from the lacunary faces of the polyoxotungstates with Dy–O bond lengths in the range 2.201(15)–2.373(18) Å. The third Dy in each triangle has an additional aqua ligand ($Dy\text{–}OH_2 > 2.5$ Å) expanding its coordination environment to capped trigonal-prismatic. The degree of protonation of the hydroxo bridges was established by bond-valence sum considerations,[45] with calculated charges on the oxygen atoms between 1.1 and 1.5. The Dy-O(H)-Dy angles are in the range 146.9(9)–154.5(8)°. The 3d–4f heterometallic cationic sub-units $\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}^{7+}$ closely resemble the $\{Ce^{IV}_3Mn^{IV}_2\}$ moiety in $[\{P_2W_{15}O_{56}\}_6\{Ce_3Mn_2(\mu_3\text{-}O)_4(\mu_2\text{-}OH)_2\}_3\text{-}(\mu_2\text{-}OH)_2(H_2O)_2\text{-}(PO_4)]^{47-}$.[15] Each comprise two Co^{II} centers and three Dy^{III} ions, giving a trigonal-bipyramidal core with the Co^{II} cations at the apices. The metal centers are linked by six μ_3-OH groups (confirmed from BVS analysis,[45] giving oxygen charges in the range 1.10–1.14) over each $\{Dy_2Co\}$ triangular face. Each Dy^{III} has eight-coordinate, distorted square-antiprismatic geometry composed of four oxygen donors from μ_3-

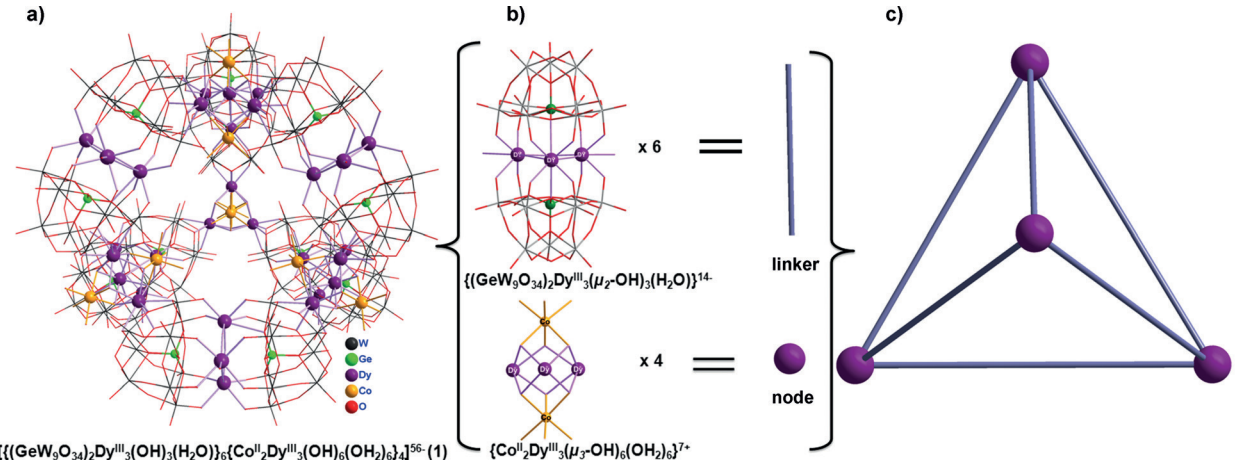

Figure 2. Combined wireframe/ball-and-stick representation of **1**: a) $[Dy_{30}Co_8Ge_{12}W_{108}O_{408}(OH)_{42}(OH_2)_{30}]^{56-}$ (**1**). b) Representations of the building blocks of **1**. The tetrahedral building units in **1** formed by connection of the six $\{(GeW_9O_{34})_2Dy^{III}_3(\mu_2\text{-}OH)_3(H_2O)_2\}^{14-}$ units via four $\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}^{7+}$ heterometallic units in **1**. c) Giant tetrahedral geometry of **1**. Color code: W gray, Co orange, Dy purple, Ge green.

OH ligands and four oxido bridges around a square W_4 face of a $[GeW_9O_{34}]^{10-}$ unit and Dy–O lengths in the range 2.320-(17)–2.470(17) Å. The Co centers have distorted octahedral geometry from three μ_3-OH groups and three terminal water molecules with Co–O distances between 2.076(16) and 2.121-(17) Å. The Dy-O-Dy and Dy-O-Co angles range between 102.9(7)° and 104.6(6)°. This assembly of four $\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}^{7+}$ and six $\{(GeW_9O_{34})_2Dy^{III}_3(\mu_2\text{-}OH)_3(H_2O)\}^{14-}$ sub-units results in a giant hollow heterometallic tetrahedral cluster with a side length of ca. 3.2 nm (Figure 2) and a central cavity of about 1.3 nm diameter. The faces' central holes (partially plugged by Cs^+ ions) of ca. 1.0 nm diameter lead to the central cavity. Na^+ ions link the giant tetrahedra within the crystal. The remaining countercations and solvent waters are heavily disordered.

Direct-current (dc) magnetic susceptibility studies of polyanion **CsCoNa-1** were carried out in an applied magnetic field of 100 Oe between 300–1.8 K. The χT versus T data, where χ is the molar magnetic susceptibility, are shown in Figure 3. At 300 K, the experimental χT value of **CsCoNa-1** (383.0 $cm^3\,K\,mol^{-1}$) per molecule is lower than the expected value of 451.4 $cm^3\,K\,mol^{-1}$ for 30 Dy^{III} metal ions (S = 5/2, L = 5, $^6H_{15/2}$, $g = 4/3$,) and 14 Co^{II} (S = 3/2, $g = 2$), probably resulting from weak antiferromagnetic interactions within the molecules. Upon lowering the temperature, the χT product is almost constant until about 120 K, after which it continuously decreases to reach 222.1 $cm^3\,K\,mol^{-1}$ at 1.8 K. This gradual decrease on lowering the temperature may result from the depopulation of the sub-states, the high anisotropy of the paramagnetic metal centers and/or weak antiferromagnetic interactions. The field dependence of magnetization at very low temperatures shows a relatively fast increase of magnetization below 10000 Oe and then a gradual increase without clear saturation up to 70000 Oe reaching a value of 178.8 μ_B (Figure 3, inset). This behavior is indicative of significant anisotropy within the system.

As a further probe of the dynamic properties of this system, ac susceptibility measurements were performed under zero dc field. The observed out-of-phase signals (about 15 % of the in-phase signals) give a clear indication of slow relaxation of the magnetization below 8 K (Figure 4 a,b) and the in-phase and out-of-phase signals are frequency-dependent. In an attempt to suppress quantum tunneling relaxation of the magnetization, small dc fields of 500–2500 Oe were applied (Supporting Information, Figure S6) but with no real effect on the relaxation mode, suggesting that the process is not influenced by quantum effects at 1.8 K and above. The relaxation dynamics were additionally investigated using micro-SQUID measurements and show clear hysteresis effects below 1.3 K at 0.14 $T\,s^{-1}$ with visible steps on the M vs. μ_0H data (Figure 4 c,d), confirming the presence of slow relaxation of the magnetization with the expected resonant quantum tunneling

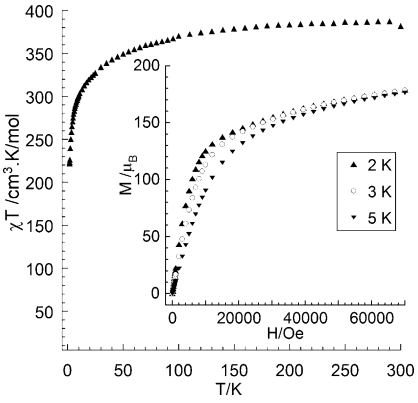

Figure 3. Plot of χT vs T for **CsCoNa-1** at an applied field of 0.01 T. Inset: Plots of M vs H for **CsCoNa-1** at the indicated temperatures.

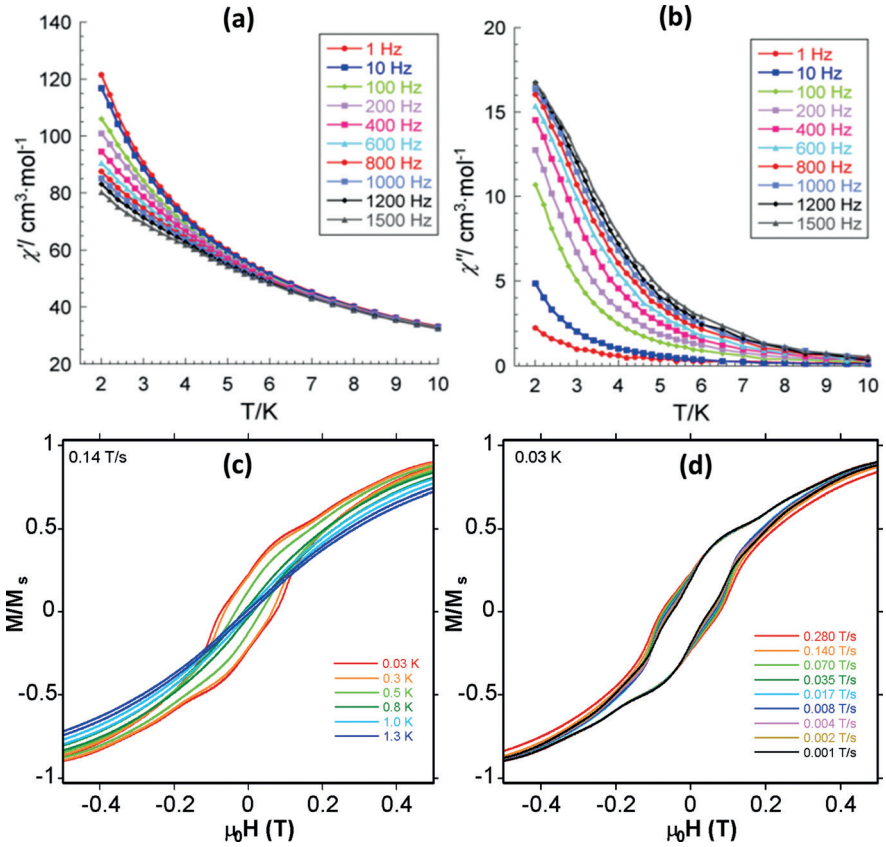

Figure 4. Temperature dependence of the a) in-phase and b) out-of-phase component of the ac magnetic susceptibility for **CsCoNa-1** in zero dc field. c) Magnetization (M) vs. applied field (μ_0H) for a single crystal of compound **CsCoNa-1**. The resulting hysteresis loops are shown in the temperature range 1.3–0.03 K at a field scan rate of 0.14 $T\,s^{-1}$. d) Magnetization (M) vs. applied field (μ_0H) hysteresis loops of **CsCoNa-1** at the indicated field sweep rates and a fixed temperature of 0.03 K.

and temperature- and sweep-rate-independent nature of the coercive field typical for a SMM system. Thus, at temperatures lower than 0.3 K, the width of the hysteresis loop is essentially temperature-independent, indicating the existence of a quantum regime where the relaxation of the magnetization takes place via quantum tunneling.

In conclusion, for the first time, a giant 3d–4f- and 4f-containing heterometallic POM has been obtained by a self-assembly synthesis. It contains two different clusters familiar from coordination cluster chemistry, namely a 3d–4f $\{Co^{II}_2Dy^{III}_3(\mu_3\text{-}OH)_6(OH_2)_6\}^{7+}$ and a 4f $\{Dy^{III}_3(\mu_2\text{-}OH)_3(H_2O)\}^{6+}$ unit. Both are stabilized by the same POM framework. These embedded coordination clusters endow the system with SMM properties. Furthermore, the compound contains the largest number of 4f ions of any POM reported to date. This work demonstrates that the key to isolating such a heterometallic 3d–4f-POM nanocluster lies in finding the reaction conditions that favor the formation of the component 3d–4f building blocks and the accompanying self-assembly reaction to give the hybrid 3d–4f-POM system. The extension of this family of POMs to other 3d and 4f centers is currently in progress.

Experimental Section

Synthesis of **CsCoNa-1**: $CoCl_2{\cdot}6H_2O$ (0.106 g, 0.445 mmol) was dissolved in H_2O (20 mL). Solid $Na_{10}[A\text{-}\alpha\text{-}GeW_9O_{34}]{\cdot}18H_2O$[46] (0.60 g, 0.21 mmol) was added and stirred until a clear pink solution was obtained. Then 0.30 mL of 1 M $Dy(NO_3)_3{\cdot}5H_2O$ (0.131 g, 0.299 mmol) was added to this solution in small portions. The resultant mixture was stirred for about 5 min, and solid LiOH (0.008 g, 0.334 mmol) was added, raising the pH from ca. 6.3 to ca. 7.8. This mixture was heated and stirred at 80 °C for 1 hour. The resulting precipitate was allowed to settle, followed by filtration and addition of 0.05 mL of 1 M CsCl solution to the filtrate. Slow evaporation at room temperature led to pink crystalline **CsCoNa-1** after about three weeks, which was isolated by filtration and dried in air. Yield 70 mg (10 % based on W). IR (2 % KBr pellet): $\tilde{\nu} = 938$ (m), 800 (s), 669(s), 539 (m), 482 (m), 423 (w), 407 cm^{-1} (w). Elemental analysis (%) calcd Cs 4.28, Na 1.58, Co 1.90, W 45.72, Ge 2.01, Dy 11.22; found: Cs 4.13, Na 1.46, Co 1.86, W 45.80, Ge 1.94, Dy 11.50.

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Keywords: dysprosium · inorganic synthesis · polyoxometalates · self-assembly · single-molecule magnets

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